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(21)Application number : **08-356003** (71)Applicant : **JAPAN STORAGE BATTERY CO LTD**
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(54) MANUFACTURE FOR SEALED LEAD STORAGE BATTERY**(57)Abstract:**

PROBLEM TO BE SOLVED: To obtain a sealed lead storage battery in which deterioration of active material for a positive electrode is prevented and its life time performance and stability is enhanced, by starting a battery jar formation of an electrode within a specific time after liquid injection using a positive electrode plate made by adding a specific amount of tin or tin compound to a positive electrode active material.

SOLUTION: In a sealed lead storage battery, Pb-Ca based alloy is used for a positive electrode grid, and metal tin or tin compound is added to active material for a positive electrode in advance so that tin in the amount of 0.5-5% by weight of active material for a positive electrode is made to exist. Time allowed to leave the electrode as it is injecting electrolytic solution into the sealed lead storage battery is set for 0.1-3 hours, most suitably 1 hour, before a battery jar formation is carried out. If the time after liquid injection is less than 0.1 hour, since the formation is started before the electrolytic solution is impregnated in the entire electrode plate, performance becomes insufficient from the beginning. If the time is within 0.1-3 hours, tin is seldom deposited. Since hydrogen overvoltage of tin is low in comparison with lead, if it is deposited on the negative electrode plate, charging efficiency lowers.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention aims at addition of the improvement in the life performance especially the tin to a positive active material, or its compound protecting degradation of a positive active material, and attaining improvement and stabilization of a sealed type lead accumulator of a life performance about the sealed type lead accumulator which used the Pb-calcium system alloy for the positive-electrode grid.

[0002]

[Description of the Prior Art] There are a retainer formula cell which is used for the sealed type lead accumulator present most widely and which contacted positive and the negative-electrode board in detailed fiberglass-mat separator, a gel formula cell which is used centering on Europe for many years and which gelled the electrolytic solution by colloidal silica, and a ***** silica formula cell by which development is furthered in recent years and which between plates and the circumference of a group of electrode were filled [cell] up with the granulation-like silica, and infiltrated the electrolytic solution into the silica.

[0003]

[Problem(s) to be Solved by the Invention] The quite short thing is known compared with it of the liquid type cell by which these sealing cells use the Pb-calcium system alloy grid for the positive electrode, therefore the cycle life used Sb alloy grid for the conventional positive electrode. One of the cause of this is because a lead-sulfate layer (the so-called barrier layer) generates to a positive-electrode grid / active material interface. The technology of adding tin is in a positive active material as one of the cure of the for many years. If tin is added, it is said that it is said that the conductivity of the corrosion layer of a grid / active material interface is raised etc., and an effect is in improvement in a life performance.

[0004] However, when the above-mentioned stannic-acid ghost was actually added, improvement in a performance might be carried out and a life performance became bad on the contrary, it was. When this cause was investigated, by the cell which carried out the capacity fall, tin was eluted from the positive electrode at an early stage, it deposited to the negative-electrode board, the charging efficiency of a negative-electrode board fell, and the lead sulfate was being accumulated mostly. Moreover, when are investigated statistically and the battery-case Chemicals method (method which performs plate Chemicals where a group of electrode is put in into a battery case) as a Chemicals method of the present lead cell with this common phenomenon is used, it turns out many things and that it happens when neglect time until it goes into Chemicals after pouring in further is long. This battery-case Chemicals method is a method which must be for the cost reduction of a cell, and its improvement on condition of this method is indispensable.

[0005]

[Means for Solving the Problem] In the sealed type lead accumulator which used the Pb-calcium system alloy for the positive-electrode grid, the manufacture method of this invention sealing type lead accumulator is a cell manufactured especially by the battery-case Chemicals method, and it is characterized by carrying out time to an after [pour] battery-case Chemicals start within 3 hours for 0.1 hours or more while it adds metal tin or a tin compound beforehand to a positive active material and making it exist as an amount of tin. [0.5% / per positive-active-material weight / or more] [5.0% or less of them]

[0006]

[Embodiments of the Invention] They carry out neglect time until it carries out battery-case Chemicals within 1 hour the optimal after pouring the electrolytic solution in a cell for 0.2 hours or more for less than 3 hours for 0.1 hours or more while 0.5% - the 5.0% per positive-active-material weight of the manufacture methods of the sealed type lead accumulator by this invention uses a Pb-calcium system alloy for a positive-electrode grid, they add metal tin or a tin compound beforehand to a positive active material and making them exist as an amount of tin. By doing in this way, the life performance of a sealed type lead accumulator is remarkably improvable.

[0007] An example of the result is shown in the following examples.

[0008]

[Example] the sulfuric-acid tin solution which put sulfuric-acid tin into the water used for paste ****, and it was made to distribute -- per active material weight -- each -- the lead paste which carried out 0.1% (B), 0.5% (C), 1% (D), 2% (E), 5% (F), and 7% (G) addition be filled up with metal tin conversion into the grid which consists of a Pb-0.1%calcium-1.5%Sn alloy, and the positive-electrode board From these ten positive-electrode boards, 11 paste formula negative-electrode boards of 1.7mm thickness, and detailed fiberglass-mat separator, the retainer formula sealing cell of abbreviation 63Ah(3hR)-12V was learned and manufactured to the usual process. In addition, the cell (A) using the conventional standard plate which has not added

sulfuric-acid tin was manufactured collectively.

[0009] after 3 minutes after these cells perform predetermined clysis according to a conventional method -- after (a) and 6 minutes -- battery-case Chemicals of 64 hours was performed to (f) by 7A after ((c) and 1 hour) after (b) and 12 minutes ((e) and 5 hours) ((d) and 3 hours) Then, life test was performed after measuring 1 / 3CA service capacity at 30 degrees C first. Life test was 40 degrees C, and after it discharged in 80% of rating with 1 / 3CA current, it was performed on the general conditions of charging by constant-voltage-constant-current system.

[0010] First, although the result of initial capacity was shown in drawing 1 , except for 0.05 hours and the case of being extremely short, the difference by neglect time did not have the neglect time after pouring in. Although there was quite little capacity in the case of 0.05 hours, since the electrolytic solution had not fully sunk into a plate, this is considered because Chemicals was inadequate. Moreover, when the addition of sulfuric-acid tin increased, the inclination which initial capacity increases a little was seen. although the life performance showed the result to drawing 2 , having suited the improvement in a life was the case where the neglect time to battery-case Chemicals was less than 3 hours for 0.1 hours or more, after pouring in, when the addition of tin was 0.5 - 5% That it was the most effective was the case where neglect time was 1 or less hour for 0.2 hours or more.

[0011] Since Chemicals was begun before the electrolytic solution penetrated through the whole plate, it is considered to originate in the performance having been inadequate from the first stage that whose life performance was not good when the neglect time after pouring in was less than 0.1 hours.

[0012] Moreover, when a tin addition was 7%, it was not based on the neglect time after pouring in, but the capacity fall was carried out at an early stage.

[0013] Although the result which analyzed the amount of tin which disassembled the cell of the same composition and was being accumulated to the negative-electrode board after the battery-case Chemicals end is shown in drawing 3 in order to clarify the reason a capacity fall becomes early, when the difference in the above-mentioned life performance and the neglect time after that a capacity fall is large when especially the amount of tin exceeds 5%, or pouring in are 5 hours Although 0.5% - 5.0% of the amount of tin was added, and there was almost no deposit of tin as well as the result of life test when the neglect time from pouring in to Chemicals was less than 3 hours for 0.1 hours or more When neglect time was 5 hours, or when a tin addition exceeded 5%, the amount of tin which deposited to the negative-electrode board had increased considerably. If a hydrogen overvoltage deposits to a negative-electrode board compared with lead for a low reason, as for tin, it is known that a charging efficiency will fall. For this reason, it is considered that whose degradation of the cell which had many amounts of deposits of tin was large.

[0014] It is PbO₂ why the neglect time after pouring in is related to elution of tin although not carried out clearly. Although ion, such as tin, is adsorbed PbSO₄ It has the property of being hard to adsorb. during the neglect time after pouring in the basis from which elution of tin becomes easy to take place during the neglect after pouring in in order that such a lot of lead sulfates that the sulfuric acid which is the electrolytic solution causes PbO in a plate and an intense reaction and is not considered by the usual charge and discharge in a plate may generate -- *****

[0015] In addition, in this example, although sulfuric-acid tin was used as a tin compound, even if it added similarly and examined metal tin and the tin oxide, to the result, it was practically equal.

[0016]

[Effect of the Invention] The life performance of a sealed type lead accumulator is remarkably improved by starting battery-case Chemicals within 3 hours after pouring in for 0.1 hours or more in the cell using the positive-electrode board which was described above and with which this invention added 0.5 - 5% of tin, or the tin compound by metal tin conversion to the positive active material like, and the standpoint of utilization of a sealed type lead accumulator to the industrial value is very large.

[Translation done.]